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(54) Process for production of maleic anhydride.

(57) Process for production of maleic anhydride comprising contacting n-butane-rich feed consisting essentially of n-butane, molecular oxygen and ballast gas with oxidation catalyst in a heat transfer medium-cooled, tubular reaction zone in which catalyst is graded in terms of reactivity such that reactivity increases to compensate for decreased reactant concentrations; removing effluent from the reaction zone; recovering maleic anhydride from the effluent; and recycling a major portion of the remaining effluent to the reaction zone.

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PROCESS FOR PRODUCTION OF MALEIC ANHYDRIDE

BACKGROUND OF THE INVENTION

5   This invention relates to the catalytic, vapor phase oxidation of n-butane to maleic anhydride. More particularly, the invention relates to an improved process for production of maleic anhydride wherein (1) a n-butane-rich oxidation feed is oxidized to

10   maleic anhydride in a heat transfer medium-cooled, tubular reaction zone, containing a fixed bed of catalyst graded in terms of reactivity, at relatively low per pass conversions of n-butane, (2) reactor effluent is withdrawn from the reaction zone and a

15   major portion of maleic anhydride is separated therefrom, and (3) a major portion of the effluent remaining after separation is recycled to the reaction zone.

    Catalytic, vapor phase oxidation of n-butane to maleic anhydride in heat transfer medium-cooled,

20   tubular reaction zones is well-known. Typically, a gaseous feed comprising molecular oxygen, n-butane and ballast gas is passed over a fixed bed of oxidation catalyst in one or more reaction tubes at temperatures of about 300° to about 650°C. and pressures

25   of about 10 to about 75 psia. The oxidation reaction is highly exothermic and, in order to maintain the desired reaction zone temperature, heat transfer medium, such as an oil or molten salt, is circulated around the reaction tube or tubes. Typically, temperature

30   of the heat transfer medium is adjusted to provide adequate cooling at the hottest point of the reaction zone. Effluent, typically comprising maleic anhydride, by-product oxygenated hydrocarbons, inert gases and unreacted n-butane and oxygen, is withdrawn from the

35   reaction zone and maleic anhydride is substantially separated therefrom.

At present, known commercial processes for producing maleic anhydride from n-butane can be characterized as once-through, air oxidation processes in that air is used as the source of molecular oxygen and, owing to the nitrogen content of air, levels of nitrogen in the reaction zone effluent build up to such an extent that recycle of effluent, with or without separation of nitrogen from unreacted n-butane, is economically impractical. In view of the flammability of mixtures of n-butane and air, concentrations of n-butane in a once-through, air oxidation feed typically are limited to about 1.8 mole%, and even this is slightly within the flammable region. As a result of such limitations on feed n-butane, the amount of maleic anhydride that can be produced per unit of reaction zone capacity is limited. Further, due to the impracticality of recycling unreacted n-butane, the same typically is discarded such that the amount of maleic anhydride produced per amount of n-butane consumed is lower than would be desirable.

In an attempt to improve productivity and n-butane consumption, it has been proposed to employ oxidation feeds containing higher concentrations of n-butane than typically are used in the above-described once-through, air oxidation processes and/or to recycle reaction zone effluent. For example, U.S. 3,899,516 (Dickason) discloses that space time yields and catalyst selectivity to maleic anhydride can be improved through the use of a feed containing n-butane and substantially pure (at least 95%) molecular oxygen in a molar ratio of at least 1:4, i.e., at least 20 mole% n-butane and less than 80 mole% oxygen in the feed. Commonly assigned U.S. 3,904,652 (Frank) discloses the use of feeds containing greater than 1.7 mole% n-butane, 3 to 13 mole% oxygen, and 70 to 95 mole% inert gas, preferably nitrogen, in conjunction with 30 to 70% per pass conversions of n-butane and

recycle of reactor effluent after separation of maleic anhydride in order to attain improved selectivity to maleic anhydride and ultimate conversions of n-butane. Similarly, U.S. 4,044,027 (Anderson et al.), which is directed primarily to improving product quality and yield by rapid cooling of reactor effluent so as to avoid decomposition of maleic anhydride and formation of color bodies, discloses the use of feeds containing at least 1.5 mole% n-butane and less than 20 mole% oxygen in conjunction with less than 50% per pass conversion and recycle of a portion of the reactor effluent after separation of maleic anhydride and at least some unreacted n-butane therefrom. W. German Offen. 2,544,972 (Hoechst) discloses a process for producing maleic anhydride from mixed butane isomers wherein a butane and air feed is oxidized, followed by removal of effluent from the reaction zone, separation of maleic anhydride from the effluent, recycle of 75 to 98% of the effluent remaining after separation to the reaction zone with addition of make-up air and butanes, adsorption of butanes from the remaining 2 to 25% of the effluent on active carbon, desorption of butanes with fresh air and charging of the butane-laden air to the reaction zone.

Despite the improvements reported in the above-described patents, the same are not entirely satisfactory from the standpoint of operation of the heat transfer medium-cooled reaction zone. As noted hereinabove, temperature of the heat transfer medium is determined on the basis of the temperature at the hottest point of the reaction zone. That point, also referred to as "hot spot," is located at the point at which the oxidation rate is maximum and the reaction is most exothermic. Given the positive dependency of reaction rates on reactant concentrations, reaction zone hot spot typically is located near the feed end of the zone because that is where reactant concentra-

tions are highest. In the above-described butane-
rich processes, feed end reaction rates are even great-
er than in typical air oxidation processes due to
increased n-butane concentrations. Above a certain
concentration of n-butane, heat of reaction cannot be
removed due to poor heat transfer in the reaction
zone. As a result, catalyst damage and/or thermal
runaway of the oxidation reaction can occur. Even if
the n-butane concentration is not so high as to cause
a thermal runaway, attempts to remove heat of reaction
from the reaction zone feed end by adjustment of heat
transfer medium temperatures can lead to problems
downstream from the feed end. Thus, reactants are
consumed as they progress from the feed end of the
reaction zone to the exit end with the result that
reactant concentrations, and accordingly reaction
rates and the amount of heat liberated, decrease.
While the heat transfer medium provides adequate cool-
ing in the vicinity of the reaction zone hot spot,
the decreased amounts of heat liberated downstream
from the feed end typically are insufficient to compen-
sate for the degree of cooling provided near the feed
end. Thus, downstream from the feed end of the reac-
tion zone, reaction rates are limited not only by
decreased reactant concentrations, but also by exces-
sive cooling. As a result, productivity suffers.

It has been proposed to improve temperature control
and operation in various processes involving exothermic
reactions by employing a reaction zone in which cata-
lyst activity varies along the length of the zone and
such proposals may be of interest with respect to the
present invention. Thus, British 721,412 (Chem Pat-
ents) discloses oxidation of olefins, and particularly
ethylene, in reaction tubes immersed in cooling medium
and packed with supported silver catalyst in such a
manner that activity increases from the inlet to the
outlet of the tubes. Dilution of effluent remaining

after removal of product followed by recycle of the diluted effluent also is disclosed. According to the patentee, the use of a graded catalyst results in increased productivity and allows for sustained opera-

5 tion without hot spot formation; however, there is no suggestion that grading of the catalyst bed can be employed to allow for operation on the hydrocarbon-rich side of the flammability zone, nor is it disclosed to employ graded catalyst as a means for improving

10 productivity. Further, results in the silver-catalyzed oxidation of ethylene cannot be readily translated to processes for oxidation of n-butane to maleic anhy-dride.

G. F. Froment, Industrial and Engineering Chemistry,

15 59 (2), pp. 18-27 (1967) proposes a two-dimensional model for hydrocarbon oxidations in fixed bed, tubular reactors and suggests that hot spot can be eliminated and average reaction zone temperature can be increased by appropriate dilution of catalyst with inert packing

20 in the early stages of the catalyst bed.

Caldwell and Calderbank, British Chemical Engineer-ing, 14 (9) pp. 1199-1201 (1969) discuss the aforesaid problems of temperature control in tubular reactors and propose dilution of catalyst in the vicinity of

25 the reaction zone hot spot as a means for attaining increased conversions without making the reaction zone more sensitive to variations in operating con-ditions. The authors also postulate an equation for calculating the catalyst dilution, as a function of

30 temperature and conversion, required to achieve desired temperature gradients.

Calderbank, Caldwell and Ross, Proceedings of the Fourth European Symposium on Chemical Reaction Engineering, Pergamon Press, Oxford, pp. 93-106 (1971)

35 present one- and three-dimensional models of exothermic

catalytic reactions carried out in fixed-bed reactors containing graded catalyst.

Calderbank and Caldwell, _Chemical Reaction Engineering, Advances in Chemistry Series_, 109 ACS, Washington D.C., pp. 38-43 (1972) discuss oxidation of o-xylene to phthalic anhydride in tubular reactors containing graded catalyst.

Smith and Carberry, _The Canadian Journal of Chemical Engineering_, 53, pp. 347-349 (1975), although silent with respect to grading of catalysts, disclose the use of partially impregnated catalysts, primarily in conjunction with the oxidation of naphthalene to phthalic anhydride, and conclude that improved yields, higher average reaction zone temperatures and decreased catalyst consumption can result.

Despite the teachings of the aforesaid British patent and the theory and mathematical relationships presented in the literature references, the same do not disclose or suggest the use of a graded catalyst bed to permit smooth operation on the hydrocarbon-rich side of the flammability zone nor as a means for permitting economically practical recycle in the production of maleic anhydride from n-butane. The references also fail to disclose actual reactivity gradients useful in oxidation of a given feed to a given product under given conditions. Further, the specific processes addressed by the references, e.g., oxidation of ethylene to ethylene oxide, o-xylene to phthalic anhydride and naphthalene to phthalic anhydride, are sufficiently different from oxidation of n-butane to maleic anhydride as to preclude direct application of the references' teachings and theory to n-butane oxidation. Thus, for example, for a given volume of gas, operation at hydrocarbon concentrations at the lower explosive limits results in evolution of twice as

much heat in the case of n-butane oxidation as in the case of oxidation of o-xylene to phthalic anhydride. Accordingly, heat removal requirements in the former are more severe.

5   From the foregoing, it can be appreciated that it would be desirable to provide a process for production of maleic anhydride wherein the advantages of a n-butane-rich oxidation feed can be better exploited. It is an object of this invention to provide such a

10   process. A further object of the invention is to provide for increased productivity per unit of reaction zone capacity in the production of maleic anhydride from n-butane. A further object of the invention is to provide for improved utilization of n-butane.

15   Another object of the invention is to provide a process wherein recycle of reaction zone effluent is made economically practical. A still further object of the invention is to provide a process that can be operated safely on the hydrocarbon-rich side of the

20   flammability envelope. A further object is to provide a process that can be implemented in conventional once-through, air oxidation facilities without loss of substantial capacity. Other objects of the invention will be apparent to persons skilled in the art from

25   the following description and the appended claims.

    We have now found that the objects of this invention can be attained by contacting a n-butane-rich oxidation feed with oxidation catalyst at relatively low per pass conversions of n-butane in a heat transfer

30   medium-cooled, tubular reaction zone in which the catalyst is graded in terms of reactivity, with recycle of a major portion of maleic anhydride-free reaction zone effluent to the reaction zone. Advantageously, the use of a n-butane-rich feed in conjunction with

35   graded catalyst results in improved productivity of maleic anhydride as compared to typical air oxidation processes and n-butane-rich processes using ungraded

catalyst. Further, grading of the catalyst bed results in a more uniform temperature profile over the effective length of the reaction zone such that reaction zone capacity is better utilized. In addition, opera-
5   tion at relatively low per pass conversions can give improved selectivities to maleic anhydride, and this in combination with recycle of unreacted n-butane can result in improved yields of maleic anhydride. Ulti- mate conversions of n-butane also are improved. As
10   compared to conventional, once-through, air oxidation processes, operation according to this invention can give up to twice the throughput for a given reaction zone capacity, with decreased catalyst consumption due to grading of the catalyst bed.

15   DESCRIPTION OF THE INVENTION

Briefly, the present invention provides a process for producing maleic anhydride which comprises (A) contacting a feed consisting essentially of about 2 to about 10 mole% n-butane, about 8 to about 20 mole%
20   molecular oxygen and a balance of inert gas or gases with oxidation catalyst in a heat transfer medium- cooled, tubular reaction zone maintained under oxida- tion conditions effective to provide a relatively low per pass conversion of n-butane, said catalyst being
25   graded along at least a portion of the effective length of the reaction zone from minimum reactivity nearest a feed end of the reaction zone to maximum reactivity nearest an exit end of the reaction zone; (B) with- drawing from the exit end of the reaction zone an
30   effluent comprising maleic anhydride, by-product oxy- genated hydrocarbons, inert gases, and unreacted oxygen and n-butane; (C) separating a major portion of maleic anhydride and by-product oxygenated hydrocarbons from the reaction zone effluent; (D) removing from the
35   effluent remaining after recovery of maleic anhydride and oxygenated hydrocarbon by-products a purge stream at a rate substantially corresponding to the rate of

build-up of inert gases in the reaction zone; and (E) recycling effluent remaining after removal of the purge stream to the reaction zone with addition of make-up gas comprising n-butane and molecular oxygen.

5   In greater detail, a typical heat transfer medium-cooled, tubular reaction zone employed according to this invention comprises one or more hollow tubes, preferably with length to diameter ratios ranging from about 25 to about 500, such tubes being encased

10   within a shell containing circulating heat transfer medium. The tubes preferably are constructed of carbon steel or stainless steel although other materials having a high degree of mechanical strength, corrosion resistance and chemical inertness also are suitable.

15   The shell that encases the tube or tubes can be constructed from any suitable material, but preferably is made of a carbon steel. The shell is provided with heating means, for example, an external electric coil or heater, to heat the heat transfer medium to

20   the desired start-up temperature. Cooling means, such as a steam boiler, also are provided to maintain the heat transfer medium at the desired temperature during oxidation. Circulation of heat transfer medium around the tube or tubes is conveniently accomplished

25   through the use of a stirrer, a pump and baffle arrangement, or other suitable means.

Heat transfer media useful according to this invention are well-known to persons skilled in the art and, in general, are materials that remain in the

30   liquid state at process temperatures and have a relatively high thermal conductivity. Examples of useful media include various heat transfer oils and salts, such as nitrates and nitrites of alkali metals, the salts being preferred due to their higher boiling

35   points. A particularly preferred heat transfer medium is a eutectic mixture of potassium nitrate, sodium

nitrate and sodium nitrite which not only has a desirably high boiling point, but also, a sufficiently low freezing point that it remains in the liquid state even during periods of reaction zone shutdown.

Catalyst is loaded into the reaction tube or tubes in such a manner that reactivity increases over at least a portion of the effective reaction zone length from minimum reactivity nearest the feed end of the reaction zone to maximum reactivity nearest the exit end. For purposes hereof, effective reaction zone length is defined as the catalyst-containing portion of the reaction zone. Preferably, effective length is at least about 75% of overall length, with any remaining length forming one or two substantially dead, e.g., catalyst-free, zones at the feed and/or exit ends of the reaction zone. More preferably, effective reaction zone length makes up about 80 to about 100% of overall length. As between feed end and exit end dead zones, the former is preferred because it can serve as a preheating zone for the oxidation feed introduced into the reaction zone.

Preferably, the entire effective length of the reaction zone is graded from minimum reactivity nearest the feed end to maximum reactivity nearest the exit end. However, it also is contemplated to grade only a portion of the effective length of the reaction zone from minimum reactivity nearest the feed end to maximum reactivity nearest the exit end. For example, proceeding from the feed end of the reaction zone to the exit end, a first portion of the effective reaction zone length can have high or intermediate reactivity and the remainder of the effective length can be graded from minimum to maximum reactivity. The initial high or intermediate reactivity zone preferably is relatively short and can give beneficial results in that the same can serve as a preheating zone for the oxidation feed. Such a reactivity gradient is illustrated

in Figure 4 and further described hereinbelow. It
also is contemplated to grade the effective length
from minimum to maximum reactivity over a first segment
and provide an intermediate or low reactivity zone at
5 the exit end of the reaction zone although this is
not a preferred embodiment because the benefits as-
sociated with providing maximum reactivity at the
area of minimum reactant concentration are reduced.
These configurations also can be combined such that
10 only a central portion of the effective length is
graded from minimum reactivity nearest the feed end
to maximum reactivity nearest the exit end. In that
case, reactivity decreases from the segment of the
effective length nearest the reaction zone feed end
15 to the minimum reactivity portion of the central por-
tion, increases across the central portion, and de-
creases from the maximum reactivity portion of the
central portion to the lower reactivity portion nearest
the exit end.
20   That portion of the effective reaction zone length
that is graded from minimum reactivity nearest the
feed end to maximum reactivity nearest the exit end
can be graded continuously and/or in stages. Ideally,
reactivity increases continuously from minimum to
25 maximum reactivity; however, from a practical stand-
point, it is more convenient to provide two or more
reactivity zones or stages along the portion of the
effective reaction zone length to be graded from mini-
mum to maximum reactivity. Preferably, the number of
30 zones ranges from two to about 20, with about three
to about eight being more preferred from the standpoint
of attaining a relatively uniform temperature profile,
and accordingly, high productivity, without incurring
excessively high catalyst loading costs.
35   For a given process, precise location, length and
relative reactivities of the various zones will vary
depending on a variety of factors, such as overall

and effective reaction zone lengths, production rate, choice of catalyst and reaction conditions, and can be determined by experimentation in accordance with the examples appearing hereinbelow. Preferably, the minimum reactivity zone nearest the feed end extends over about 10 to about 50% of the effective reaction zone length and reactivity ranges from about 10 to about 75% of that in the maximum reactivity zone nearest the exit end, with the remainder of the effective length containing one or more zones of increasing reactivity. For purposes hereof, reactivity can be expressed on a relative basis with a 100% value being assigned to the maximum reactivity segment of that portion of the effective reaction zone length graded from minimum reactivity nearest the feed end to maximum reactivity nearest the exit end. Correspondingly higher or lower values can be assigned to other segments based upon the rate of n-butane conversion therein relative to the rate in the 100% zone.

Any suitable means for providing the desired reactivity gradient is contemplated according to this invention. Most simply, pelleted oxidation catalyst is employed, with the desired gradation being accomplished by blending of catalyst pellets with an inert solid. Suitable inert solid diluents include materials which do not adversely affect catalyst performance in the oxidation reaction and which are at least roughly similar to the catalyst pellets in terms of size and shape, so that a substantially uniform flow of gas through the catalyst bed is ensured. Specific examples of useful solid diluents include silica, alumina and carborundum pellets. A continuous reactivity gradient can be provided by feeding catalyst pellets and inerts to the reaction tube or tubes using separate variable speed feeders. Staged gradient can be provided by batchwise blending of catalyst pellets and inerts in appropriate amounts.

A related method of achieving the desired reactivity gradient is to employ a supported catalyst in which the proportion of support decreases, and correspondingly, the proportion of active catalyst increases, from the minimum to maximum reactivity zones. Partial impregnation of support with catalyst can give particularly good results in that selectivity typically is improved. Suitable supports are described in detail hereinbelow.

A third method for grading the catalyst bed involves the use of different catalyts in the individual reactivity zones, with catalyst of maximum reactivity being employed in the maximum reactivity zone nearest the exit end, catalyst of lowest reactivity being employed in the minimum reactivity zone nearest the feed end, and one or more catalysts of intermediate reactivity being used in any intermediate reactivity zone or zones. Particularly good results are attained when the lower reactivity catalysts have high selectivities.

Another method for achieving the desired gradient is to use blends of catalysts of varying reactivities containing varying proportions of the individual catalysts in the different reactivity zones.

Of course, various combinations of the above or other techniques also can be employed to attain a reactivity gradient tailored to specific process equipment or requirements.

Oxidation catalysts useful according to this invention are known to the art, and, in general, are materials capable of catalyzing the oxidation of n-butane to maleic anhydride under oxidation conditions. Examples of useful catalysts are discussed hereinbelow, it being understood that the same are for purposes of illustration and guidance in the practice of the invention.

-14-

One class of catalysts useful according to the invention is the phosphorus-vanadium-oxygen complex catalysts. Such catalysts typically contain about 0.5 to about 5 atoms of phosphorus per atom of vanadium

5 and are prepared by reaction of compounds of phosphorus and vanadium in aqueous or organic medium followed by heating of the resulting solid. Suitable phosphorus compounds include phosphorus pentoxide, phosphoric acid, orthophosphorus acid, phosphorus trichloride,

10 phosphorus trioxide and triethyl phosphate, and suitable vanadium compounds include vanadium oxalate, vanadium formate, ammonium metavanadate, vanadyl trichloride, metavanadic acid, vanadium sulfate and vanadium phosphate. Reaction of such compounds is

15 conducted in an aqueous or organic medium to form a solid reaction product which is isolated by evaporation of supernatant liquid. Subsequently, the solid is activated by heating at about 300° to about 600°C. and ground and/or pelleted. Activation can be conducted

20 before or after grinding and/or pelleting. Optionally, the catalyst is blended with a suitable inert support, for example, alpha alumina or silicon carbide, prior to use. Further details with respect to such phosphorus-vanadium-oxygen complex catalysts are found in

25 U.S. 3,293,268 (Bergman et al.) and U.S. 3,907,707 (Raffelson et al.) which are incorporated herein by reference.

Phosphorus-vanadium-oxygen complex catalysts also can be prepared by fusion of phosphorus pentoxide

30 into a vanadium pentoxide matrix as disclosed in U.S. 3,907,833 (Slinkard et al.).

A second class of useful catalysts is the metal-promoted phosphorus-vanadium-oxygen complexes. Such catalysts typically contain about 0.5 to about 5 atoms

35 of phosphorus per vanadium atom and, in addition, from about 0.001 to about 5 atoms of at least one metal promoter per vanadium atom. Useful promoters

include the alkali and alkaline earth metals, scandium, lanthanum, yttrium, cesium, neodymium, samarium, titanium, zirconium, hafnium, niobium, tantalum, chromium, tungsten, molybdenum, manganese, rhenium, iron,

5   cobalt, nickel, palladium, copper, silver, zinc, cadmium, aluminum, gallium, indium, silicon, germanium, tin, antimony, bismuth, tellurium, thorium and uranium. In general, one or more of these promoters is incorporated into a phosphorus-vanadium-oxygen

10   complex before, during or after the complex-forming reaction. Such catalysts can be either supported or unsupported. Further details with respect to such catalysts are found in the following patents which are incorporated herein by reference:

15   U.S. 3,862,146 (PVO promoted with Zr, Bi, Cu, Li);

U.S. 3,832,359 (PVOFe complex);

U.S. 3,905,914; 3,931,046 and 3,932,305 (PVOZr complexes);

U.S. 3,980,585 (PVO promoted with Te, Zr, Ni, Ce, W,

20   Pd, Ag, Mn, Cr, Zn, Mo, Re, Sm, La, Hf, Ta, Th, Co, U, or Sn, and in addition an alkali or alkaline earth metal);

U.S. 4,062,873 and 4,064,070 (PVOSi complex);

U.S. 4,147,661 (PVO promoted with W, Sb, Nb, and/or

25   Mo);

U.S. 4,151,116 (PVO promoted with "post-deposited" Mg, Ca, Se, Y, La, U, Ce, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Ga, In, Si, Ge, Sn, Bi, Sb, or Te; optionally, Ti, Zn, Hf, Li, Mg, Ca, Fe, Co, Ni,

30   Cu, Sn, Bi, U, a rare earth metal, Cr, Cd or Al is incorporated into the complex prior to post-deposition of promoter);

U.S. 4,152,338 (PVO promoted with Nb, Cu, Mo, Ni, Co and Cr, preferably containing, in addition, Ce,

35   Nd, Ba, Hf, U, Ru, Re, Li or Mg);

U.S. 4,152,339 (PVOCu promoted with Te, Zr, Ni, Ce, W, Pd, Ag, Mn, Cr, Zn, Mo, Re, Sm, La, Hf, Ta,

Th, Co, U or Sn, preferably also containing an
alkali or alkaline earth metal);

U.S. 4,153,577 and 4,158,671 (PVO promoted with Cu,
Mo, Ni, Co, Cr, Nd, Ce, Ba, Y or Sm);

5   British 1,403,395 (PVOTi optionally containing WO_3
and/or MoO_3).

A third group of catalysts is that wherein the
primary metal is other than vanadium. For example,
U.S. 2,691,660 discloses butane oxidation catalysts

10   comprising molybdenum, and cobalt or nickel oxides,
and optionally, a promoter selected from boron, phos-
phorus and vanadium oxides, silicon, tungsten, tita-
nium, beryllium, zirconium, chromium and uranium.
U.S. 3,928,392 discloses butane oxidation catalysts

15   comprising oxides of antimony, molybdenum, and nickel,
cobalt, copper or zinc. U.S. 4,065,468 discloses
butane oxidation catalysts comprising the combined
oxides of antimony, molybdenum, and vanadium or iron,
optionally containing, in addition, one or more oxides

20   of aluminum, boron, tellurium, chromium, cobalt, nick-
el, copper, bismuth, phosphorus, titanium or tungsten.

The presently preferred catalysts for use according
to this invention are the metal-promoted phosphorus-
vanadium-oxygen complex catalysts such as those accord-

25   ing to U.S. 3,862,146.

Oxidation according to this invention is carried
out in the above-described heat transfer medium-cooled,
tubular reaction zone containing graded catalyst by
introducing a feed consisting essentially of about 2

30   to about 10 mole% n-butane, about 8 to about 20 mole%
molecular oxygen and a balance of inert gas or gases
into the feed end of the reaction zone maintained
under conditions such that a relatively low per pass
conversion of n-butane is attained. An effluent,

35   comprising maleic anhydride, by-product oxygenated
hydrocarbons, unreacted n-butane and oxygen, and inert
gas or gases, is withdrawn from the exit end of the

reaction zone and maleic anhydride, and oxygenated
hydrocarbon by-products are substantially separated
therefrom after which the remaining effluent is sepa-
rated into a purge stream, that is removed at a rate

5   that substantially compensates for the build-up of
inerts in the reaction zone, and a recycle stream
that is recycled to the reaction zone with addition
of make-up gas comprising n-butane and molecular oxy-
gen.

10   The composition of the oxidation feed employed
according to this invention is important not only
from the standpoint of attaining desirable yields of
maleic anhydride, but also with respect to safe re-
action zone operation. As indicated hereinabove, the

15   feed preferably contains levels of n-butane on the
hydrocarbon-rich side of the flammability envelope.
Irrespective of n-butane concentration, feed gas con-
centrations should be adjusted to avoid formation of
flammable mixtures. Generally, at n-butane concentra-

20   tions in the upper portion of the aforesaid range,
oxygen concentrations in the higher portion of the
aforesaid range are employed. Conversely, at lower
n-butane concentrations, lower oxygen levels should
be employed.

25   Further detail with respect to feed composition
is provided in Figure 1 of the drawing which illus-
trates the flammability envelope for mixtures of
molecular oxygen, n-butane and a balance of nitrogen
at room temperature at atmospheric pressure. Point 1

30   is illustrative of feed compositions in typical once-
through, air oxidations, while points 2-4 illustrate
feed compositions employed according to this invention.
Points 3 and 4 illustrate feeds containing preferred
levels of n-butane and oxygen in that the same are on

35   the n-butane-rich side of the flammability zone, and
accordingly, result in improved productivity. It
should be recognized that the Figure 1 flammability

curve is specific to gaseous mixtures in which the
inert gas is nitrogen. When carbon dioxide is present
in the inert gases, such as in the preferred embodi-
ments of this invention, the flammable region decreases
5   somewhat. Elevated temperatures and pressures expand
the flammable region.

The n-butane used according to this invention
preferably is substantially pure, i.e., at least about
96%. However, it also is contemplated to include up
10 to about 20 mole% of one or more other oxidizable C_4
hydrocarbons such as isobutane, butenes or butadienes
in the feed.

The molecular oxygen source used according to the
invention has a substantial effect on productivity.
15 Substantially, i.e., at least 95%, pure oxygen is
preferred because the amount of ballast gas required
to avoid formation of a flammable mixture in the reac-
tion zone is supplied in whole by the recycle stream
in which case the purge stream removed from the reac-
20 tion zone effluent prior to recycle need only be great
enough to compensate for the levels of carbon oxides
produced during oxidation. On the other hand, if
oxygen of lower purity is used, a larger purge stream
is required in order to compensate not only for forma-
25 tion of carbon oxides as a result of the oxidation,
but also for the inerts introduced with the molecular
oxygen.

The ballast gas supplied to the reaction zone
will vary depending on the molecular oxygen source.
30 If substantially pure oxygen is used, the ballast gas
provided by the recycle stream is predominantly a
mixture of carbon monoxide and carbon dioxide. The
molar ratio of carbon monoxide to carbon dioxide is a
function of catalyst choice, but generally ranges
35 from about 0.5:1 to about 2.5:1. In addition to mini-
mizing purge stream requirements, the use of sub-
stantially pure oxygen and attendant presence of carbon

dioxide in the ballast gas facilitates temperature
control due to the high heat capacity of carbon dioxide.   If the molecular oxygen source to be used is
air, the ballast gas, of course, will contain sub-
stantial amounts of nitrogen. Similarly, if a mixture
of molecular oxygen and one or more inert gases consti-
tutes the molecular oxygen source, the ballast gas
will include the inert gas or gases introduced with
the oxygen.   If ballast gas other than that provided
in the recycle stream and/or that introduced to the
reaction zone with the oxygen must be introduced to
the reaction zone to adjust the feed composition, it
is preferred to use nitrogen, carbon monoxide, carbon
dioxide or mixtures thereof.   Mixtures of carbon monox-
ide with carbon dioxide containing enough of the latter
to reduce the flammability zone are more preferred.

Preferably, the oxidation feed contains from about
3 to about 8 mole% n-butane, about 10 to about 18 mole%
molecular oxygen and about 74 to about 87 mole% ballast
gas.   When substantially pure oxygen is used as the
molecular oxygen source, ballast gas preferably com-
prises about 30 to about 50 mole% carbon monoxide,
about 35 to about 55 mole% carbon dioxide and less
than about 1 mole% nitrogen.   If air is the molecular
oxygen source, ballast gas preferably comprises about
70 to about 85 mole% nitrogen, up to about 5 mole%
carbon dioxide and about 1 to about 10 mole% carbon
monoxide.   For a feed containing 5.5 mole% n-butane,
14 mole% oxygen and a balance of carbon monoxide and
carbon dioxide in a molar ratio of about 1.1:1, a
safety margin of 1.2 mole% n-butane or 1.6 mole% oxygen
exists with respect to the flammability limit.

The oxidation feed is introduced into the feed
end of the reaction zone which is maintained under
reaction conditions effective to attain relatively
low per pass conversions of n-butane.   For purposes
hereof, per pass conversion is defined as 100% times

the number of moles of n-butane oxidized divided by
the number of moles of n-butane in the feed. Prefer-
ably, the per pass conversion rate ranges from about
15 to about 70%, and more preferably, from about 30

5   to about 55% in order to attain high ultimate con-
versions with good selectivity to maleic anhydride.
Reaction conditions include temperature, pressure,
space velocity, and others as discussed in greater
detail hereinbelow.

10   Reaction zone temperature is sufficiently high to
attain reasonable reaction rates, but not so high as
to damage the oxidation catalyst or promote undesirable
side reactions. Preferred temperatures range from
about 300° to about 650°C., with about 350° to about

15   500°C. being more preferred. It is desirable to pre-
heat the oxidation feed to within about 100°C. of
reaction temperature prior to passing the feed over
that portion of the catalyst bed that is graded from
minimum to maximum reactivity.

20   Reaction zone pressure is not critical although
from a practical standpoint it is preferred to oper-
ate at about 10 to about 70 psia (about 0.7 to about
5 kg/cm^2).

The oxidation feed is fed to the reaction zone at

25   a rate such that relatively low per pass n-butane
conversions are attained. Preferably, volumetric
space velocity of the feed ranges from about 1000 to
about 3000/hour. More preferably, volumetric space
velocity ranges from about 1500 to about 2500/hour as

30   the same results in desirable productivity without
excessive pressure drop from the feed end to the exit
end of the reaction zone. At volumetric space veloci-
ties of about 1500 to about 2500/hour, per pass n-
butane conversions typically range from about 30 to

35   about 50%. Contact time in the reaction zone varies
depending on space velocity and pressure and typically
ranges from about 0.5 to about 4 seconds.

From the exit end of the reaction zone there is
withdrawn an effluent comprising maleic anhydride,
by-product oxygenated hydrocarbons, inert gas or gases,
and unreacted n-butane and oxygen. Primary by-product
5   oxygenated hydrocarbons include acetic and acrylic
acids which typically are produced in amounts somewhat
greater than in conventional once-through, air oxida-
tions. The effluent is passed to a separation zone
in which maleic anhydride and by-product oxygenated
10   hydrocarbons are substantially recovered. The remain-
ing effluent is divided into purge and recycle streams
and the latter is returned to the reaction zone togeth-
er with make-up gas comprising oxygen and n-butane.

Separation of maleic anhydride and by-product
15   oxygenated hydrocarbons from the reaction zone effluent
can be accomplished by any suitable means. For exam-
ple, the effluent can be scrubbed with an aqueous
liquid, e.g., an aqueous solution of maleic acid, and
the resulting scrubber solution dehydrated to convert
20   maleic acid to the anhydride. Acetic and acrylic
acids, also removed from the effluent by scrubbing,
pass overhead during dehydration and can be recovered
by fractionation, extraction or other suitable means.

Another method for recovering maleic anhydride
25   from the effluent is to condense a portion of the
anhydride out of the effluent prior to scrubbing of
effluent and dehydration of maleic acid. Partial
condensation prior to scrubbing can give beneficial
results in terms of maleic anhydride yields in that
30   less of the anhydride is converted to acid, and accord-
ingly, less acid is available for irreversible isomeri-
zation to fumaric acid. Further, reduced levels of
maleic and fumaric acids are advantageous because the
acids are solids under recovery conditions and can
35   plug processing equipment.

Another suitable method for recovery of maleic
anhydride and by-product oxygenated hydrocarbons is

to contact the effluent with an organic solvent having low absorption capacity for water and high absorption capacity for maleic anhydride, and then strip the maleic anhydride from the solvent. In this manner,

5   hydrolysis of maleic anhydride to the acid is substantially avoided thus resulting in improved yields of maleic anhydride. Useful absorbants include a variety of organic solvents, specific examples of which are found in U.S. 3,891,680 (Katsumoto et al.)

10   and U.S. 4,118,403 (White).

Effluent remaining after substantial recovery of maleic anhydride and by-product oxygenated hydrocarbons, comprising inert gases and unreacted n-butane and oxygen, is divided into a purge stream and a re-

15   cycle stream. The purge stream is removed at a rate that substantially compensates for the buildup of inerts in the reaction zone. The precise rate of removal depends upon a variety of factors, such as source of molecular oxygen, production rate, reaction

20   zone capacity, choice of catalyst and oxidation conditions, as can be appreciated by persons skilled in the art. When substantially pure oxygen is used as the source of molecular oxygen, preferred purge rates range from about 1 to about 20 mole% of the effluent

25   gas. If air is the molecular oxygen source, purge rates of about 20 to about 75 mole% are preferred.

After removal of the purge stream, the remaining effluent is recycled to the reaction zone. As noted hereinabove, if substantially pure oxygen is used as

30   the molecular oxygen source, only n-butane and oxygen need be supplied to the reaction zone as make-up gases because the recycle stream will provide adequate levels of inert gases for the oxidation feed. If air or low purity oxygen is the molecular oxygen source, inert

35   gas or gases will accompany the make-up oxygen.

A preferred manner of operating in accordance
with the present invention is described in greater
detail in conjunction with the drawing wherein:

Figure 2 illustrates a process diagram; and

5   Figures 3 and 4 illustrate preferred catalyst
gradient profiles.

Referring to Figure 2, on startup n-butane and
air are metered from n-butane and air sources (not
shown) to feed line 13 via lines 5 and 7 respectively.

10   The feed is introduced into the feed end of reactor
15 which is shown with a portion of its wall cut away
to reveal reaction tubes 17 and 19. The reactor also
contains circulating molten salt (not shown). A por-
tion of the wall of tube 19 is cut away to reveal

15   centrally extending thermowell 21 which is used for
temperature measurement. Tubes 17 and 19 are loaded
with catalyst (not shown) graded in terms of reac-
tivity.

Preferred reactivity gradient profiles are shown

20   in Figures 3 and 4 wherein reaction zone length is
plotted on the abscissa--with 0% corresponding to the
feed end and 100% corresponding to the exit end--and
relative reactivity is plotted on the ordinate. Ac-
cording to the Figure 3 profile, the entire effective

25   length of the reaction zone is graded from minimum
reactivity nearest the feed end to maximum reactivity
nearest the exit end. A dead zone, with 0% reactivity,
makes up the first 10% of the overall reaction zone
length and serves as a preheating zone for the oxida-

30   tion feed. The reactivity profile illustrated in
Figure 4 differs from that of Figure 3 in that overall
and effective reaction zone lengths are equal with
only a portion of the effective length being graded
from minimum reactivity nearest the feed end to maximum

35   reactivity nearest the exit end. The first 15% of
the reaction zone is an intermediate reactivity zone

and, like the dead zone in Figure 3, serves as a pre-heating zone.

Referring again to Figure 2, the air and n-butane feed passes into contact with catalyst in tubes 17 and 19 under oxidation conditions whereby n-butane is oxidized to maleic anhydride and by-products. There is a pressure drop from the feed end to the exit end such that reactor effluent passes out of the exit end of the reactor to scrubber 25 via line 23.

In the scrubber, effluent is contacted counter-currently with an aqueous solution of maleic acid that is pumped to the top of the scrubber from scrubber solution tank 29 via lines 31 and 33, pump 35, line 37, cooler 39 and line 40. Maleic anhydride and by-product oxygenated hydrocarbons from the effluent are absorbed by the scrubber liquid and pass by gravity through line 27 to the scrubber solution tank. The use of an aqueous scrubber solution results in sub-stantial hydrolysis of maleic anhydride to maleic acid. Most of the maleic acid collected in the scrub-ber solution tank passes to a product recovery and purification section (not shown) via line 31.

Gaseous effluent from scrubber 25, comprising inert gases, unreacted n-butane and oxygen, and any maleic anhydride and by-product oxygenated hydrocarbons not removed by the scrubber liquid, pass overhead from scrubber 25 via line 41 to condenser 43 wherein vaporized scrubber liquid passing overhead is condensed out of the effluent.

From the condenser, effluent passes to filter 53 via line 45 which also feeds to purge line 47. The purge line is equipped with back pressure valve 49, which regulates pressure in the product recovery sec-tion. The purge stream passes from the back pressure valve through line 51 to an incinerator or other dis-posal equipment (not shown). The remaining effluent from line 45 passes to filter 53 wherein solids, for

example, maleic and fumaric acids, are removed from
the gas stream.

The filtered effluent then passes to compressor
57 via line 55. Compressed effluent is conveyed to
5   recycle feed line 11 via recycle line 59.

As the process proceeds, levels of inerts supplied
to the reactor in the recycle gas build up, and, when
the inerts reach an appropriate proportion of the
total feed to the reactor, preferably about 70 to
10   about 95 mole%, the air feed preferably is discontinued
and oxygen is fed to the reactor via lines 9 and 13
in order to reduce purge stream requirements and there-
by increase the amount of n-butane recycled to the
reactor. In the alternative, the air feed is simply
15   continued. It also is contemplated to use oxygen
instead of air on start-up.

The following examples illustrate the present
invention, it being understood that the same are for
purposes of illustration and not limitation.

20   GENERAL EXPERIMENTAL PROCEDURE

(A) Molten Salt-Cooled Tubular Reaction Zone

The reaction zone used in all runs was a vertical,
stainless steel tube having a length of 8 feet (2.44
meters) and an inner diameter of 1.049 inches (2.66
25   cm). A thermowell having an outer diameter of 0.375
inch (0.953 cm) was provided along the axis of the
reaction tube. The thermowell contained a travelling
thermocouple assembly consisting of eight individual
thermocouples spaced at one foot intervals. During
30   oxidation runs the reaction tube was immersed in a
bath of molten salt, consisting of a eutectic mixture
of sodium nitrate, sodium nitrite and potassium ni-
trate, contained in a stainless steel shell having a
length of 8 feet (2.44 meters) and an inner diameter
35   of 4 inches (10.2 cm). The salt bath was heated with
an electric coil located at the exterior of the shell.
Nitrogen was bubbled through the salt bath at a rate

of about 1 SCFH to provide circulation around the
reaction tube.

(B) Graded Catalyst Bed

The catalyst employed in all runs was a zinc-
promoted phosphorus-vanadium-oxygen complex containing
1.19 atoms phosphorus and 0.2 atoms zinc per atom of
vanadium and prepared substantially according to
Example I of U.S. 3,862,146. The catalyst was used
in the form of cylindrical pellets 3/16 inch (0.48
cm) long by 3/16 inch (0.48 cm) diameter. As loaded,
catalyst bulk density was 67.4 lbs/ft^3 (1.08 g/cm^3).

Catalyst gradation was accomplished by blending
weighed amounts of catalyst and alumina pellets
(identified by the Norton Company trademark "Denstone")
of the same shape and size as the catalyst pellets.
Bulk densities of the catalyst-Denstone blends were
the same as that of the pure catalyst. The reaction
zone had a 1 foot (0.3 meter) feed end dead zone and
a 1/2 foot (0.15 meter) exit end dead zone, both of
which contained only Denstone pellets. Effective
length was 6 1/2 feet (1.98 meter), the entirety of
which was graded from minimum reactivity nearest the
feed end to maxium reactivity nearest the exit end
according to the following profile:

ZONE	LENGTH (ft.)	WEIGHT (g) CATALYST	WEIGHT (g) DENSTONE	REACTIVITY (%)
I	2.6 (0.79 m)	208	208	50
II	1.3 (0.40 m)	131	77	63
III	1.3 (0.40 m)	166	42	80
IV	1.3 (0.40 m)	208	0	100

(C) Feed Gases

Commercial grade n-butane was used in all runs.
Typical analysis, reported in mole %, was as follows:

Ethane	0-0.05%
Propane	0.09-0.54%
i-Butane	1.63-1.77%
n-Butane	96.7-96.84%
Butene-1	0-0.038%
i-Butene	0-0.028%
i-Pentene	0.06-1.04%
t-Butene-2	0-0.067%
c-Butene-2	0.040-0.74%
C_5 and higher	0-0.480%

Oxygen, when used, was extra dry grade having a minimum purity of 99.6%. Air, when used, had a maximum moisture content of 0.3%.

(D) Operation

For all runs, DP cells with integral orifices were used to feed oxygen, air and recycle gas. n-Butane was metered to the reaction tube using a DP cell equipped with a 0.069 inch (0.18 cm) inner diameter, 90 feet (27.4 meter) long capillary, which aided in maintaining laminar flow and a suitable pressure drop. The n-butane assembly was installed in a 150°F. (66°C) oven to ensure reproducibility of feed rates.

Prior to introduction into the reaction tube, the feed gases were mixed and heated to 350°F (177°C). The feed then was fed to the top of the reaction tube which was maintained at 15 psig (1.05 kg/cm^2). Feed composition, reaction conditions and feed rate are shown in the tables appearing hereinbelow.

Effluent exited the reaction tube at its bottom, which was under pressure of 14 psig (0.98 kg/cm^2), and was passed through a filter to remove entrained catalyst particles. The filtered effluent then was passed through a pressure control valve and from there to a primary scrubber consisting of a 2 1/2 foot (0.76

m) long, 4 inch (10.2 cm) inner diameter glass pipe filled with 1/2 inch (1.3 cm) ceramic saddles. In the primary scrubber, the effluent was contacted countercurrently with aqueous maleic acid. Most of the maleic anhydride in the effluent was removed in the primary scrubber. Scrubbed effluent was passed from the primary scrubber to a secondary scrubber which consisted of a 2 foot (0.61 m) long, 4 inch (10.2 cm) inner diameter glass pipe filled with 3/8 inch (0.95 cm) ceramic saddles. The bottom half of the secondary scrubber was filled with water while the top half served as a disentrainment chamber. Scrubbed effluent from the primary scrubber was bubbled through the water resulting in further removal of maleic anhydride and by-product oxygenated hydrocarbons.

Scrubbed effluent was divided into purge and recycle streams by passing a portion of the effluent through a back pressure valve maintained at about 5 psig (0.35 kg/cm^2) and from there to a wet test meter which measured the purge stream flow rate. In recycle runs, the recycle stream was filtered, compressed to 25 psig (1.76 kg/cm^2) in a diaphragm compressor and returned to the reaction tube. In comparative runs operated on a once-through basis, the entire scrubbed effluent was passed to the wet test meter. Space velocity through the tube was regulated by adjustment of the recycle gas flow rate.

(E) Analyses and Yield Calculations

For all runs, feed and effluent gases were analyzed using a Fisher-Hamilton Model 1200 gas chromatograph with dual columns.

Volumetric Space Velocities (abbreviated "VSV" hereinbelow) were determined by dividing volumetric feed rates at 0°C. and 1 atmosphere by reaction zone volume.

Maleic anhydride yields were determined by potenti-
ometric amine titration of scrubber solution samples.

Maleic anhydride productivity was determined by
dividing the calculated weight of recovered maleic
5   anhydride by the product of (1) duration and (2) the
combined weight of catalyst and diluent.

Selectivity to maleic anhydride was calculated by
dividing maleic anhydride molar yields by the number
of moles of n-butane converted and multiplying by
10   100%. Selectivity based on total hydrocarbon feed
can be calculated by multiplying selectivities based
on n-butane by 0.96.

EXAMPLE 1

A series of oxidations was conducted over the
15   course of several days. Feed compositions, mode of
operation, reaction conditions and results are shown
in TABLE 1.

TABLE 1

RUN NO.	1	2	3	4
MODE	OTA[1]	RA[2]	RA	RA
FEED (mole %)				
n-C_4	1.46	2.89	3.00	3.97
O_2	20.6	12.1	12.7	12.9
CO	0	2.07	1.90	1.74
CO_2	0.03	1.58	1.54	1.43
N_2	77.0	80.4	79.9	79.0
TEMP (°F)				
Hot Spot	826	830	826	829
Salt Bath	767	757	754	745
VSV (hr^{-1})	1510	1640	1640	1630
DURATION (days)	1	1	1	2
EFFLUENT (mole %)				
n-C_4	0.38	1.53	1.58	2.47
O_2	16.4	6.31	6.45	6.21
CO	1.27	3.63	3.55	3.43
CO_2	0.90	2.76	2.87	2.82
N_2	80.1	80.4	79.9	79.0
n-C_4 CONVERSION (%)				
Per Pass	–	49.6	50.1	41.5
Overall	74.7	71.2	71.2	60.7
MAN[3]				
YIELD (wt.%)	70.2	–	68.4	59.7
PRODUCTIVITY[4]	0.0390	–	0.0534	0.0597
SELECTIVITY[5]	52.7	–	57.0	58.3

(1) In this and all subsequent tables "OTA" stands
for once-through, air oxidation.

(2) In this and all subsequent tables "RA" stands for
recycle runs using air as the molecular oxygen
source.

(3) In this and all subsequent tables "MAN" stands
for maleic anhydride.

(4) In this and all subsequent tables MAN
    Productivity is reported in grams MAN/(gram
    (catalyst + diluent)) (hour).

(5) In this and all subsequent tables MAN Selectivity
    is reported in mole %.

TABLE 1 (Cont.)

RUN NO.	5	6	7	8
MODE	RA	RA	RA	RA
FEED (mole %)				
$n-C_4$	3.99	4.28	3.04	3.54
O_2	12.9	13.0	11.7	12.1
CO	1.76	1.75	2.24	2.06
CO_2	1.44	1.45	1.78	1.67
N_2	79.0	78.6	80.3	7.97
TEMP (°C)				
Hot Spot	442	449	448	449
Salt Bath	396	394	405	402
VSV (hr^{-1})	1630	1620	1640	1620
DURATION (hr)	1	1	1	1
EFFLUENT (mole %)				
$n-C_4$	2.50	2.69	1.57	1.98
O_2	6.02	5.51	5.12	5.03
CO	3.49	3.70	4.03	3.98
CO_2	2.87	3.04	3.19	3.20
N_2	79.0	78.6	80.3	79.7
$n-C_4$ CONVERSION (%)				
Per Pass	41.2	41.2	51.2	47.4
Overall	60.1	59.0	71.9	66.1
MAN				
YIELD (wt.%)	59.5	58.7	69.3	62.1
PRODUCTIVITY	0.0596	0.0622	0.0542	0.0566
SELECTIVITY	58.7	59.5	57.1	55.7

EXAMPLE 2

Over four consecutive days a series of four runs was conducted. Details are reported in TABLE 2.

TABLE 2

RUN NO.	1	2	3	4
MODE	OTA	OTA	RA	RA
FEED (mole %)				
$n-C_4$	1.52	1.52	3.65	4.61
O_2	20.7	20.7	12.0	12.6
CO	0	0	2.15	1.92
CO_2	0.03	0.03	3.34	3.36
N_2	76.9	76.9	79.6	78.4
TEMP (°C)				
Hot Spot	443	431	446	448
Salt Bath	409	402	399	395
VSV (hr^{-1})	1510	1510	1620	1630
DURATION (hr)	3	1	1	1
EFFLUENT (mole %)				
$n-C_4$	0.32	0.40	2.08	2.93
O_2	15.9	16.2	4.72	4.57
CO	1.53	1.34	4.15	4.05
CO_2	1.14	1.01	3.34	3.36
N_2	80.2	80.1	84.7	84.1
$n-C_4$ CONVERSION (%)				
Per Pass	–	–	46.4	40.7
Overall	78.0	74.6	65.8	58.2
MAN				
Yield (wt.%)	66.0	66.1	61.5	52.6
Productivity	0.0367	0.0367	0.0553	0.0568
Selectivity	49.0	52.5	55.4	53.6

EXAMPLE 3

A third series of once-through and recycle runs using air was conducted over several days. Details are reported in TABLE 3.

TABLE 3

RUN NO.	1	2	3	4	5
MODE	OTA	RA	RA	RA	OTA
FEED (mole %)					
$n-C_4$	1.44	6.12	5.22	6.14	1.72
O_2	16.4	12.1	15.9	13.3	16.1
CO	0	1.93	1.02	1.62	0
CO_2	0.03	1.72	0.86	1.43	0.03
N_2	76.9	77.2	76.1	76.7	76.7
TEMP (°C)					
Hot Spot	433	452	455	447	430
Salt Bath	404	391	383	385	398
VSV (hr^{-1})	1510	1490	1530	1551	1510
DURATION (hr)	3	1	1	1	3
EFFLUENT (mole %)					
$n-C_4$	0.35	4.33	3.28	4.27	0.42
O_2	16.4	2.69	6.64	3.66	15.4
CO	1.34	4.47	3.52	4.17	1.58
CO_2	1.01	3.94	2.96	3.66	1.24
N_2	80.0	83.6	82.7	83.3	80.4
$n-C_4$ CONVERSION (%)					
Per Pass	–	34.6	42.1	35.9	–
Overall	76.5	49.7	51.5	49.3	76.0
MAN					
Yield (wt.%)	67.4	43.3	46.5	43.7	67.0
Productivity	0.0373	0.0540	0.0580	0.0529	0.0371
Selectivity	52.2	51.6	53.5	52.6	51.8

Comparison of the once-through-air (OTA) and re-cycle-air (RA) runs in EXAMPLES 1-3 and TABLES 1-3 shows that productivity in the latter was substantially greater than in the once-through mode although in other respects, results were generally comparable.

Due to incomplete activation of the catalyst in EXAMPLES 1-3, reaction rates were low and several brief temperature runaways occurred. Runaways were easily controlled by minor reductions in n-butane

-35-

feed rates and salt bath temperature. After the
catalyst was sufficiently activated (Example 3 Run 4)
no more runaways occurred.

EXAMPLE 4

In this example a series of recycle runs with
oxygen was followed by a once-through, air oxidation
run. Details are reported in TABLE 4.

TABLE 4

RUN NO.	1	2	3	4	5
MODE	RO[1]	RO	RO	RO	RO
FEED (mole %)					
$n-C_4$	3.17	3.04	3.44	3.84	4.83
O_2	11.8	15.6	15.3	15.5	13.6
CO	43.9	41.7	42.0	42.2	42.8
CO_2	40.4	39.0	38.5	37.7	38.2
N_2	0.68	0.62	0.80	0.68	0.55
TEMP (°C)					
Hot Spot	442	445	444	443	450
Salt Bath	406	403	401	398	397
VSV (hr^{-1})	1590	1550	1600	1610	1570
DURATION (days)	1	1	2	1	1
EFFLUENT (mole %)					
$n-C_4$	1.75	1.45	1.84	2.17	3.10
O_2	5.28	8.34	7.64	7.61	5.03
CO	47.9	46.2	46.8	47.1	48.0
CO_2	44.4	43.4	43.2	42.6	43.3
N_2	0.71	0.58	0.58	0.52	0.59
$n-C_4$ CONVERSION (%)					
Per Pass	48.0	55.1	49.9	47.3	40.3
Overall	96.7	96.6	95.6	95.3	93.8
MAN					
Yield (wt. %)	86.4	86.1	84.2	84.5	77.1
Productivity	0.0525	0.0566	0.0595	0.0637	0.0615
Selectivity	53.0	52.8	52.2	52.6	48.7

(1) In this and all subsequent tables, "RO" stands for
recycle runs using 96% pure oxygen.

TABLE 4 (Cont.)

RUN NO.	6	7	8	9
MODE	RO	RO	RO	OTA
FEED (mole %)				
n-C_4	4.90	3.65	4.00	1.48
O_2	16.5	15.3	15.9	20.7
CO	41.5	42.9	42.4	0
CO_2	36.6	37.6	37.2	0.03
N_2	0.54	0.59	0.55	76.9
TEMP (°C)				
Hot Spot	449	448	447	432
Salt Bath	392	403	401	403
VSV (hr^{-1})	1530	1910	1960	1510
DURATION (days)	3	1	1	1
EFFLUENT (mole %)				
n-C_4	3.04	2.06	2.42	0.35
O_2	7.50	8.02	8.34	16.1
CO	47.0	47.4	47.0	0.35
CO_2	42.0	42.0	41.7	1.16
N_2	0.42	0.50	0.54	80.0
n-C_4 CONVERSION (%)				
Per Pass	42.8	47.1	43.5	-
Overall	93.7	95.8	94.6	77.2
MAN				
Yield (wt. %)	75.5	79.3	82.2	61.2
Productivity	0.0634	0.0668	0.0725	0.0340
Selectivity	47.7	49.1	51.5	47.0

EXAMPLE 5

Subsequent to the runs in EXAMPLE 4 the oxidation catalyst was regenerated by passing 9 ml carbon tetra-chloride over the catalyst at 404°C in 0.077 SCFM nitrogen over a period of 15 minutes. The carbon tetrachloride and nitrogen were introduced into the exit end of the reaction tube.

Following regeneration, four recycle runs were carried out using oxygen. Details are reported in TABLE 5.

TABLE 5

RUN NO.	1	2	3	4
MODE	RO	RO	RO	RO
FEED (mole %)				
$n-C_4$	3.24	4.06	4.12	4.76
O_2	12.2	12.6	15.4	15.2
CO	46.0	45.3	43.6	43.6
CO_2	38.1	37.4	36.1	35.9
N_2	0.52	0.62	0.86	0.54
TEMP (°C)				
Hot Spot	449	449	449	450
Salt Bath	412	407	403	400
VSV (hr^{-1})	1750	1830	1950	2010
DURATION (days)	3	1	1	1
EFFLUENT (mole %)				
$n-C_4$	1.75	2.53	2.53	3.15
O_2	5.40	5.36	7.80	7.35
CO	49.9	49.7	48.2	48.4
CO_2	42.4	41.8	40.8	40.5
N_2	0.57	0.66	0.76	0.57
$n-C_4$ CONVERSION (%)				
Per Pass	49.3	41.8	42.7	38.3
Overall	97.1	95.5	94.7	93.6
MAN				
Yield (wt. %)	91.4	90.3	90.1	88.3
Productivity	0.0646	0.0721	0.0794	0.0849
Selectivity	55.8	56.0	56.4	56.0

EXAMPLE 5 and TABLE 5 illustrate a preferred manner of operating according to this invention. As can be

seen, ultimate conversions of n-butane ranging from about 94 to 97% were attained at sufficiently high selectivities that maleic anhydride yields of about 90% were achieved. Productivity in Runs 3 and 4 was

5   about double that of the once-through, air oxidation runs in previous examples.

EXAMPLE 6

Another series of recycle runs with oxygen was conducted over five consecutive days and then a once-

10   through, air oxidation was carried out.   Details are reported in TABLE 6.

TABLE 6

RUN NO.	1	2	3	4
MODE	RO	RO	RO	RO
FEED (mole %)				
n-C_4	5.24	5.36	5.18	4.83
O_2	14.2	14.4	14.2	15.2
CO	43.5	43.2	43.4	43.1
CO_2	36.5	36.6	36.6	36.3
N_2	0.57	0.48	0.52	0.54
TEMP (°C)				
Hot Spot	448	447	449	454
Salt Bath	398	398	399	398
VSV (hr^{-1})	2030	1980	1950	1970
DURATION (days)	4	1	1	1
EFFLUENT (mole %)				
n-C_4	3.69	3.78	3.56	3.19
O_2	6.42	6.55	6.35	7.35
CO	48.1	48.0	48.3	47.8
CO_2	41.1	41.1	41.3	41.1
N_2	0.68	0.51	0.49	0.54
n-C_4 CONVERSION (%)				
Per Pass	34.0	34.2	36.3	38.7
Overall	92.3	92.8	93.7	94.1
MAN				
Yield (wt. %)	82.5	82.5	82.5	82.5
Productivity	0.0794	0.0794	0.0794	0.0794
Selectivity	53.0	52.0	52.0	52.0

(Line numbers in left margin: 5, 10, 15, 20, 25)

TABLE 6 (Cont.)

RUN NO.	5	6
MODE	RO	OTA
FEED (mole %)		
n-C_4	4.73	1.52
O_2	15.7	20.7
CO	42.6	0
CO_2	36.4	0.03
N_2	0.54	76.9
TEMP (°C)		
Hot Spot	451	433
Salt Bath	399	405
VSV (hr^{-1})	1980	1510
DURATION (days)	1	3
EFFLUENT (mole %)		
n-C_4	3.08	0.37
O_2	7.72	16.0
CO	47.5	1.52
CO_2	41.1	1.16
N_2	0.60	80.0
n-C_4 CONVERSION (%)		
Per Pass	39.1	
Overall	93.4	76.6
MAN		
Yield (wt. %)	82.3	63.0
Productivity	0.0792	0.0350
Selectivity	52.2	48.7

EXAMPLE 7

Following regeneration of catalyst according to the procedure of EXAMPLE 5 a once-through, air oxidation was conducted and then five recycle runs with oxygen were carried out over five consecutive days. Details are reported in TABLE 7.

From the table it can be seen that selectivity varies somewhat depending on n-butane concentration. For the catalyst used in these examples, selectivity

was best when n-butane concentration was about 5 mole %.

TABLE 7

RUN NO.	1	2	3	4
MODE	OTA	RO	RO	RO
FEED (mole %)				
$n-C_4$	1.49	7.28	6.12	5.88
O_2	20.8	11.8	13.5	14.6
CO	0	42.3	42.6	42.0
CO_2	0.03	38.0	37.0	37.0
N_2	76.8	0.61	0.69	0.48
TEMP (°C)				
Hot Spot	430	451	451	452
Salt Bath	406	399	398	396
VSV (hr^{-1})	1510	1760	1740	1740
DURATION (days)	1	3	1	1
EFFLUENT (mole %)				
$n-C_4$	0.37	5.71	4.40	4.11
O_2	16.4	2.89	4.54	5.67
CO	1.31	47.3	48.1	47.4
CO_2	1.01	43.4	42.3	42.1
N_2	80.0	0.62	0.68	0.68
$n-C_4$ CONVERSION (%)				
Per Pass		27.4	33.6	35.4
Overall	76.2	89.4	91.6	92.1
MAN				
Yield (wt. %)	73.3	70.6	81.5	83.3
Productivity	0.0408	0.0679	0.0784	0.0805
Selectivity	57.0	46.8	52.8	53.6

TABLE 7 (Cont.)

RUN NO.	5	6
MODE	RO	RO
FEED (mole %)		
n-C_4	5.72	5.10
O_2	14.0	14.8
CO	42.3	42.5
CO_2	37.3	36.8
N_2	0.64	0.69
TEMP (°C)		
Hot Spot	448	447
Salt Bath	397	398
VSV (hr^{-1})	1840	1880
DURATION (days)	1	1
EFFLUENT (mole %)		
n-C_4	4.04	3.48
O_2	5.66	6.82
CO	47.5	47.5
CO_2	42.2	41.5
N_2	0.61	0.72
n-C_4 CONVERSION (%)		
Per Pass	34.6	36.3
Overall	92.6	92.7
MAN		
Yield (wt. %)	82.8	85.9
Productivity	0.0796	0.0826
Selectivity	53.0	54.9

EXAMPLE 8

Another series of recycle runs with oxygen was followed by a once-through run with air. Details are reported in TABLE 8.

TABLE 8

RUN NO.	1	2	3	4	5
MODE	RO	RO	RO	RO	CTA
FEED (mole %)					
n-C_4	5.66	5.53	5.24	5.34	1.46
O_2	13.4	13.7	14.3	14.2	20.8
CO	42.8	42.5	42.5	42.2	0
CO_2	37.5	37.6	37.3	37.7	0.03
N_2	0.61	0.64	0.77	0.59	76.8
TEMP (°C)					
Hot Spot	449	448	440	438	433
Salt Bath	398	398	397	395	406
VSV (hr^{-1})	1940	1950	2110	2160	1510
DURATION (days)	3	3	1	3	1
EFFLUENT (mole %)					
n-C_4	4.07	3.93	3.74	3.90	0.34
O_2	5.12	5.46	6.72	6.57	15.9
CO	48.1	47.8	47.1	46.8	0.34
CO_2	42.1	42.1	41.5	42.1	1.25
N_2	0.67	0.70	0.87	0.60	80.0
n-C_4 CONVERSION (%)					
Per Pass	32.8	33.4	32.9	31.1	
Overall	91.0	90.9	91.8	90.4	77.6
MAN					
Yield (wt. %)	81.7	80.1	84.6	80.6	62.4
Productivity	0.0792	0.0777	0.0819	0.0781	0.0347
Selectivity	53.2	52.2	54.6	52.9	47.6

From the foregoing examples and tables, it can be appreciated that operation in accordance with the present invention can result in substantial improvements over typical once-through air operations. Among these improvements are increases in reactor productivity by more than 100% in some cases and reduction in butane consumption per unit weight of product.

We claim:

1. A process for producing maleic anhydride comprising

(A) contacting a feed consisting essentially of about 2 to about 10 mole % n-butane, 8 to about 20 mole % molecular oxygen, and a balance of at least one inert gas with oxidation catalyst in a heat transfer medium-cooled, tubular reaction zone maintained under oxidation conditions effective to yield a relatively low per pass conversion of n-butane, said catalyst being graded along at least a portion of the effective length of the reaction zone so as to provide minimum reactivity nearest the feed end of the reaction zone and maximum reactivity nearest the exit end of the reaction zone;

(B) withdrawing from the reaction zone an effluent comprising maleic anhydride, by-product oxygenated hydrocarbons, carbon oxides, n-butane and oxygen;

(C) separating a major portion of maleic anhydride and oxygenated hydrocarbon by-products from said effluent;

(D) removing from the effluent remaining after recovery of maleic anhydride and oxygenated hydrocarbon by-products a purge stream at a rate substantially corresponding to the rate of buildup of inert gases in the reaction zone; and

(E) recycling effluent remaining after removal of the purge stream to the reaction zone with addition of make-up gases comprising n-butane and oxygen.

2.   The process of claim 1 wherein the molecular oxygen is substantially pure and the inert gas consists essentially of a mixture of carbon monoxide and carbon dioxide.

5   3.   The process of claim 2 wherein only a portion of the effective reaction zone length is graded from minimum reactivity nearest the feed end to maximum reactivity nearest the exit end, the remainder of the effective length being located at the feed end and

10   serving as a preheating zone for the feed.

4.   The process of claim 2 wherein the entire effective length of the reaction zone is graded from minimum reactivity nearest the feed end to maximum reactivity nearest the exit end.

15   5.   The process of claim 4 wherein the feed consists essentially of about 3 to about 8 mole % n-butane, about 8 to about 18 mole % molecular oxygen, about 30 to about 50 mole % carbon monoxide, about 35 to about 55 mole % carbon dioxide and less than about

20   1 mole % nitrogen.

6.   The process of claim 5 wherein the minimum reactivity zone nearest the feed end extends over about 10 to about 50% of the effective reaction zone length and reactivity in said zone ranges from about

25   10 to about 75% of that in the maximum reactivity zone nearest the exit end.

7.   The process of claim 1 wherein the source of oxygen is air and the inert gas contained in the feed consists essentially of nitrogen.

30   8.   The process of claim 7 wherein only a portion of the effective reaction zone length is graded from minimum reactivity nearest the feed end to maximum reactivity nearest the exit end, the remainder of the effective length being located at the feed end and

35   serving as a preheating zone for the feed.

9. The process of claim 7 wherein the entire effective length of the reaction zone is graded from minimum reactivity nearest the feed end to maximum reactivity nearest the exit end.

10. The process of claim 9 wherein the feed consists essentially of about 3 to about 8 mole % n-butane, about 10 to about 18 mole % molecular oxygen, about 1 to about 10 mole % carbon monoxide, up to about 5 mole % carbon dioxide and about 70 to about 85 mole % nitrogen.

11. The process of claim 10 wherein the minimum reactivity zone nearest the feed end extends over about 10 to about 50% of the effective reaction zone length and reactivity in said zone ranges from about 10 to about 75% of that in the maximum reactivity zone nearest the exit end.

12. The process of claim 1 wherein the oxidation catalyst comprises a phosphorus-vanadium-oxygen complex.

13. The process of claim 1 wherein the oxidation catalyst is a metal-activated phosphorus-vanadium-oxygen complex.

14. The process of any of claims 1-13 wherein grading of catalyst in terms of reactivity is accomplished by blending of catalyst with inerts.

15. The process of any of claims 1-13 wherein grading of catalyst in terms of reactivity is accomplished by partial impregnation of catalyst support.

16. The process of any of claims 1-13 wherein grading of catalyst in terms of reactivity is accomplished through the use of catalysts of varying reactivities.

17. The process of any of claims 1-13 wherein grading of the catalyst in terms of reactivity is accomplished by blending catalysts of varying reactivities.
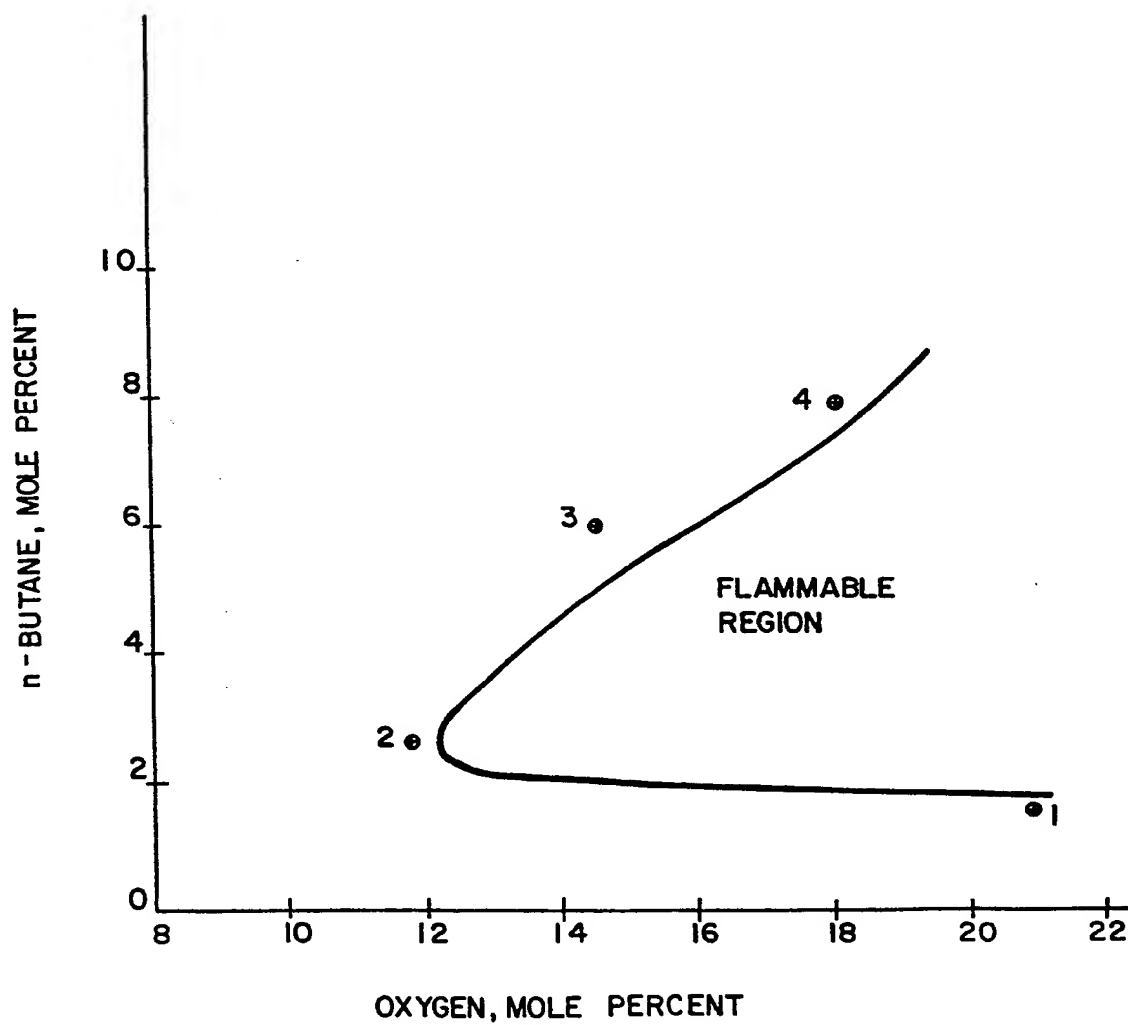
FIG. 1

FLAMMABILITY DIAGRAM FOR n-BUTANE, OXYGEN AND NITROGEN
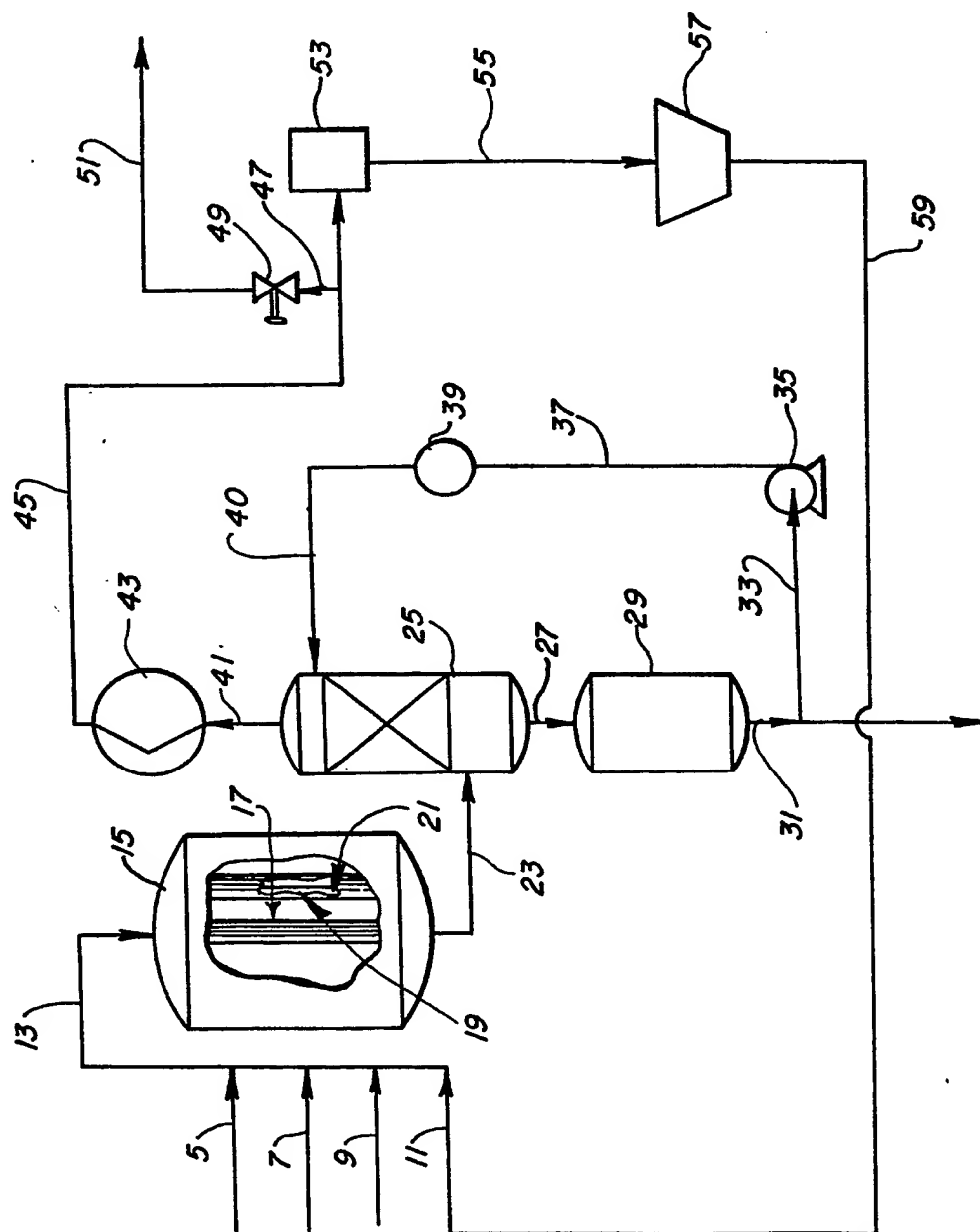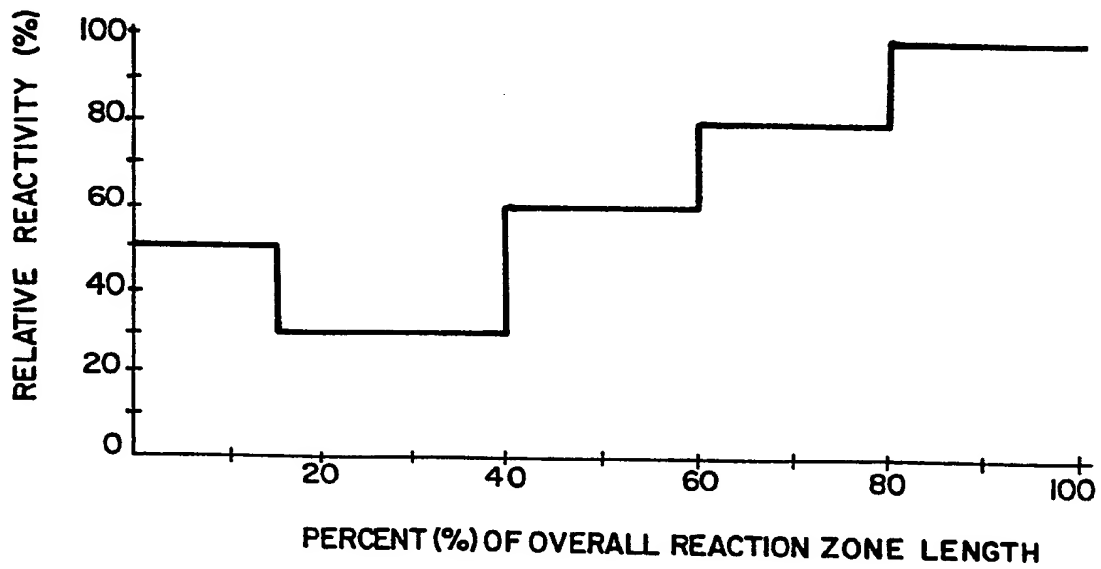
FIG. 2

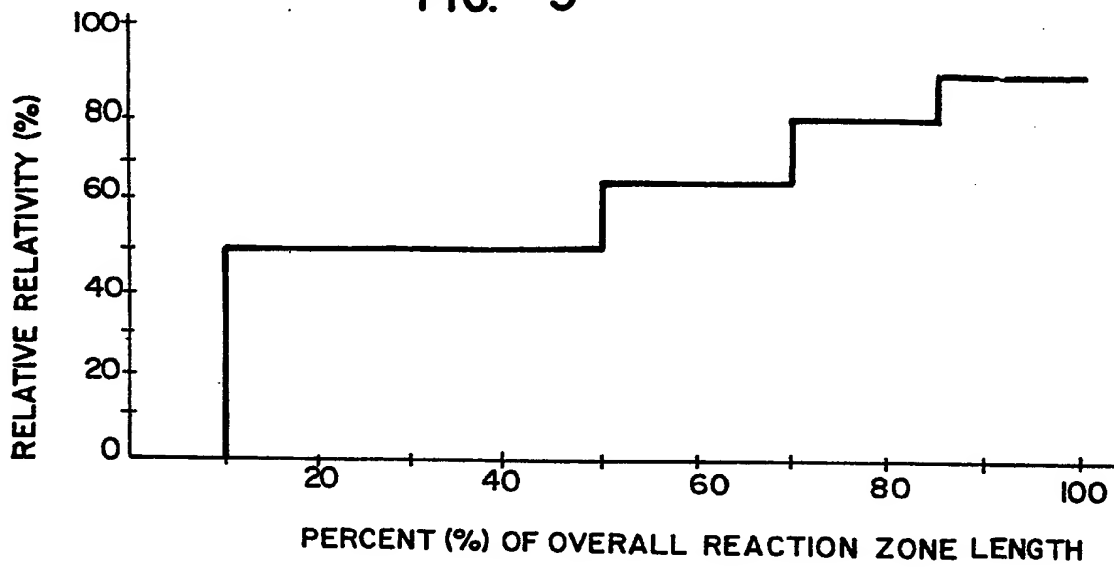0099431

FIG. 3

PERCENT (%) OF OVERALL REACTION ZONE LENGTH

PERCENT (%) OF OVERALL REACTION ZONE LENGTH

FIG. 4

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 82 30 3809

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	DE-A-2 658 191 (CHEVRON RESEARCH) * Claim 1 *	1,12	C 07 D 307/60
A	GB-A-1 528 317 (STANDARD OIL) * Claims 1, 2 ; figures 1, 2 *	1	
A,D	US-A-3 904 652 (M.E. FRANK) * Claims 1-5 *	1,2,7, 12,13	
A,D	US-A-4 044 027 (R.G. ANDERSON et al.) * Claim 1 ; abstract *	1,2,7	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 07 C 51/54
C 07 C 57/145
C 07 D 307/60

The present search report has been drawn up for all claims

Place of search BERLIN	Date of completion of the search 01-03-1983	Examiner KNAACK M

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